Effect of Pressure on the luminescence Emissions in CuGaSe$_2$

W. Shan$^a$, W. Walukiewicz, J. Wu, K.M. Yu, and J.W. Ager III

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

S. Siebentritt and N. Rega

Hahn-Meitner-Institut, 14109 Berlin, Germany

We present the results of a pressure-dependent photoluminescence (PL) study on CuGaSe$_2$ films grown on GaAs substrate by metalorganic vapor phase epitaxy. The low-temperature PL spectra of the CuGaSe$_2$ samples measured at atmospheric pressure are dominated by one near band-edge exciton luminescence line and two strong and relatively broad emissions associated with donor acceptor pairs (DAP). All the observed luminescence emission lines shift toward higher energy with increasing pressure at almost the same rate. The nearly identical pressure coefficients of the two DAP emissions as compared to that of the exciton emission confirm the suggestion that the recombination processes associated with the DAPs involve one shallow donor and two different acceptor species with different binding energies and related to two different native defects.

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$^a$ electronic mail: WShan@lbl.gov
Solar cells based on chalcopyrite absorbers Cu(In,Ga)(S,Se)$_2$ represent the most advanced thin film photovoltaic technology with laboratory cells reaching above 19% efficiency.\textsuperscript{1} The modules of Cu(In,Ga)(S,Se)$_2$ solar cells are in pilot production at several sites worldwide and large modules have reached efficiencies above 13%,\textsuperscript{2} and output power of 80W.\textsuperscript{3} Despite this technological progress, many of the fundamental properties of chalcopyrite-type semiconductors are still not fully understood. One of the poorly understood issues is the nature of the defects involved in the luminescence structures observed in Cu-rich CuGaSe$_2$ and other chalcopyrites at low temperatures.\textsuperscript{4-11}

In CuGaSe$_2$, as well as in CuInSe$_2$ and CuGaS$_2$, grown under Cu-excess, the defect related luminescence is dominated by two donor-acceptor pair (DAP) transitions, with their relative intensities dependent on the amount of Cu-excess. In CuGaSe$_2$ the transitions appear at 1.63-1.62 eV and 1.66-1.67 eV and have been attributed to involve one donor and two acceptors associated with defects. However, the microstructural origin of these defects is unclear. In particular, the question on the nature of the electronic states introduced by these defects, i.e. whether they are effective-mass like shallow state or deep localized state, is still open. So far most studies of the DAP transitions in Cu-rich CuGaSe$_2$ have been limited to temperature-dependent PL measurements. It is well known that application of hydrostatic pressure can provide important insights as how the properties of the DAP transitions depend on the band structure of the host material by changing the conduction band structure. In this letter, we present the results of an investigation into the effect of pressure on the emission properties of the luminescence spectral features observed in CuGaSe$_2$ samples.

The samples used in this work were CuGaSe$_2$ thin films grown on (001) GaAs substrates by metalorganic vapor phase epitaxy (MOVPE), at a substrate temperature of 570°C, using
cyclopentadienyl Cu triethyl phosphine, triethyl Ga and ditertiarybutyl Se as precursors. The recipes basically follow the procedure developed by Chichibu and coworkers. Detailed description of the method can be found in Refs. 8 and 12. Growth rates are low at 100nm/h to ensure a growth close to the thermodynamic equilibrium. The chemical composition of the epilayers was determined by energy dispersive x-ray spectroscopy using low energy electrons to exclude influence by the substrate. The samples are grown under Cu-excess, i.e. the integral \( [\text{Cu}] / [\text{Ga}] > 1 \). The excess Cu is accommodated in a Cu\(_8\)Se phase at the surface, as expected from the phase diagram, which can be etched. The photoluminescence spectra are not changed by the etching besides a small shift due to strain relaxation. Thus the observed PL spectra originate from the nearly stoichiometric chalcopyrite phase.

Pressure-dependent photoluminescence measurements were performed using a gasketed diamond anvil cell (DAC). In order to accommodate the dimensions of the DAC, small sample pieces with size of \( \sim 200 \times 200 \; \mu \text{m}^2 \) were prepared by mechanical polishing and cutting and then loaded into the DAC. The cell was mounted onto the cold finger of a closed cycle refrigerator and cooled down to 20 K for the measurements. The experimental setup for PL measurement consists of an Ar\(^+\) laser (4765Å) as an excitation source and a 1-m double-grating monochromator to disperse PL spectra. The PL signals were detected by a photomultiplier tube followed by a data acquisition system. The applied pressures were determined by the standard method of monitoring the shift of the ruby R1 line.

Figure 1 shows the low-temperature photoluminescence spectra taken at atmospheric pressure. The PL spectra exhibit a rich luminescence structure. Two sharp luminescence lines marked by FX and BX in the figure can be identified as near band-edge free-exciton and bound-exciton emissions, respectively. The intensity of BX peak was found to decrease with increasing
temperature much faster than that of FX as shown in Fig. 1, where the PL spectral features are plotted as a function of temperature. It became hardly resolvable when the temperature was raised above 70 K. Such effects of temperature on the luminescence intensity indicate the emission line BX resulting from radiative recombination of a bound exciton. The rapid thermal quenching implies that the exciton is bound very weakly with the localization energy of ~ 4 meV (the energy separation between FX and BX peaks); hence it is most likely bound to a neutral acceptor.

The strong emission peaks denoted as DA1 and DA2 have been attributed to the luminescence associated with donor acceptor pair transitions in the CuGaSe2. This can be readily verified by the observation of the characteristic blue shift of the emission peaks with increasing excitation power density (not shown), as well as the emergence of free-to-bound transitions marked as eA, as the sample temperature increases as shown in Fig. 1. Convincing arguments have been put forth to suggest that these two transitions most likely originate from a same donor to two acceptors with different binding energies.

Under applied pressure, these two spectral features and the exciton emissions shift toward higher energy as the CuGaSe2 band gap increases. Shown in Fig.2 are a few PL spectra recorded at selected pressures. The intensity of exciton emissions decreases gradually with pressure. This is commonly observed and can be attributed to the incrementally enhanced recombination caused by the pressure-induced defects acting as nonradiative recombination centers. On the other hand, although the overall integrated intensity of the luminescence peaks associated with DAP transitions remain nearly unchanged, the intensity ratio of the DA1 and DA2 emissions is changing with increasing pressure. The pressure-induced change in the intensity ratio is in the same manner as the intensity ratio changes with increasing [Cu]/[Ga]
ratio in Cu-rich CuGaSe$_2$. This result agrees with the inference that the luminescence spectral features are correlated to native defects.\textsuperscript{6-9} It further indicates that the acceptor levels involved in the DAP transitions may be related to two different native defects and the one responsible for the deeper acceptor level is energetically more favorable at large pressures.

In Fig. 3 we plot the peak energies of various observed emission structures as a function of pressure. The solid lines in the figure are the least-squares fits to the experimental data using the quadratic-fit function

\[ E(P) = E(0) + \alpha P + \beta P^2. \] (1)

Where $\alpha = dE/dP$ and $\beta = \frac{1}{2}d^2E/dP^2$, the energy $E$ is in eV and the pressure $P$ is in GPa. It is known that the emission lines associated with the radiative decay of free excitons or shallow bound excitons shift at the same rate as the host semiconductor band gap under hydrostatic pressure.\textsuperscript{18} The electron stays in the conduction-band edge state or in the orbit of shallow donor state associated with the conduction-band edge and the excitonic hole bound in the Coulomb field retains the symmetry of the valence-band edges. Therefore, the change of the exciton emission energy with pressure plotted in the figure provides an unmistakable signature of the direct band-gap dependence for CuGaSe$_2$. The best fits to the data yield a linear slope of 47.9 meV/GPa with a very small negative quadratic term of $-5 \times 10^{-4}$ eV/GPa$^2$ resulting in slightly sublinear pressure dependence of the band gap. The pressure coefficient of band gap of CuGaSe$_2$ epitaxial films on GaAs substrates reported here is in good agreement with those reported in other studies of bulk CuGaSe$_2$ involving absorption measurements under pressure,\textsuperscript{19,20} where a linear pressure dependence of 50 and 48 meV/P Ga was obtained at room temperature.
The pressure coefficients of the two emissions associated with the DAP transitions are almost identical, with the linear pressure coefficient $\alpha = \frac{dE}{dP} = 48.4$ and $48.5$ meV/GPa for the DA1 and DA2 emissions, respectively. The results of pressure coefficients for all the luminescence spectral features obtained in this work are listed in Table 1. It is interesting to note that the pressure dependence of the DA1 and DA2 emissions closely follow the band-gap variation of the host material under applied pressure. The small differences can be attributed to uncertainty of pressure calibration (within $\pm 0.1$ GPa), as well as the possible pressure-induced change of the exciton binding energy, which arises from an increasing electron effective mass and a decrease in the dielectric constant as the band gap increases.\textsuperscript{18,21} The nearly identical pressure coefficients of the two DAP emissions as compared to that of the exciton luminescence confirm the suggestion that only one donor and two different acceptor species with different binding energies are involved in the recombination processes associated with the DAP transitions. Furthermore, the results clearly indicate that the donor state is a shallow hydrogenic effective-mass state which is expected to strictly follow the conduction-band edge under pressure. Therefore, our results are consistent with the previously proposed model that a shallow donor rather than a deep donor is involved in the DAP transitions observed in the Cu-rich CuGaSe\textsubscript{2}.\textsuperscript{8}

In conclusion, we have studied the effect of hydrostatic pressure on the PL emission in CuGaSe\textsubscript{2} epitaxial films grown on (001) GaAs substrates by MOVPE. The pressure dependence of the exciton emission structure provides a direct measure of the pressure coefficient for the fundamental band gap of CuGaSe\textsubscript{2}. It has been found that the luminescence peaks associated with DAP transitions exhibit nearly identical pressure dependence as the exciton emissions. Our results agree with the model that the recombination processes associated with the DAP
transitions involve one shallow donor and two different acceptor species with different binding energies and related to two different native defects.

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References


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Table I. Pressure coefficients of the various emission structures observed in the CuGaSe$_2$ sample studied in this work.

<table>
<thead>
<tr>
<th></th>
<th>$E(\theta)$(eV)</th>
<th>$\alpha$(10$^{-2}$eV/GPa)</th>
<th>$\beta$(10$^{-4}$eV/GPa$^2$)</th>
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<tbody>
<tr>
<td>Exciton(FX/BX)</td>
<td>1.716/1.712</td>
<td>47.9</td>
<td>-5.05</td>
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<tr>
<td>DA1</td>
<td>1.662</td>
<td>48.4</td>
<td>-5.13</td>
</tr>
<tr>
<td>DA2</td>
<td>1.629</td>
<td>48.5</td>
<td>-4.91</td>
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Figure captions

**Figure 1.** Photoluminescence spectra of the CuGaSe$_2$ sample at several different temperatures.

**Figure 2.** PL spectra taken from the CuGaSe$_2$ sample at 25K under selected pressures.

**Figure 3.** Dependence of the energy positions on pressure for the various observed PL transitions in the CuGaSe$_2$ sample.
CuGaSe$_2$/GaAs

Energy (eV)

PL Intensity (arb.units)

12 K
25 K
50 K
62.5 K
75 K

DA2
DA1
DA2+1LO
BX
FX

eA1
eA2

Figure 1/3
Figure 2/3
Figure 3/3

CuGaSe$_2$/GaAs
20 K

Pressure (GPa)

Energy (eV)